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METHOD FOR REMOVAL OF HEAVY METAL FROM MOLTEN SALT IN IFR FUEL PYROPROCESSING*

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ABSTRACT

The pyrometallurgical process for recycling spent metal fuels from the Integral Fast Reactor (IFR) involves electrorefining spent fuel in a molten salt electrolyte (LiCl-KCl-U/$PuCl_3$) at 500°C. The total heavy metal chloride concentration in the salt will be about 2 mol %. At some point, the concentrations of alkali, alkaline earth, and rare earth fission products in the salt must be reduced to lower the amount of heat generated in the electrorefiner. The heavy metal concentration in the salt must be reduced before removing the fission products from the salt. The operation uses a lithium-cadmium alloy anode that is solid at 500°C, a solid mandrel cathode with a ceramic catch crucible below to collect heavy metal that falls off it, and a liquid cadmium cathode. The design criteria that had to be met by this equipment included the following: (1) control of the reduction rate by lithium, (2) good separation between heavy metal and rare earths, and (3) the capability to collect heavy metal and rare earths over a wide range of salt compositions. In tests conducted in an engineering-scale electrorefiner (10 kg uranium per cathode), good separation was achieved while removing uranium and rare earths from the salt. Only 13% of the rare earths was removed, while 99.9% of the uranium in the salt was removed; subsequently, the rare earths were also reduced to low concentrations. The uranium concentration in the salt was reduced to 0.05 ppm after uranium and rare earths were transferred from the salt to a solid mandrel cathode with a catch crucible. Rare earth concentrations in the salt were reduced to less than 0.01 wt % in these operations. Similar tests are planned to remove plutonium from the salt in a laboratory-scale (100-300 g heavy metal) electrorefiner.

INTRODUCTION

Electrorefining is a key step in the pyrometallurgical process that was developed to recover uranium, plutonium, and minor actinides from spent metal fuel [1,2] from the Integral Fast Reactor (IFR). The IFR is an advanced reactor concept that was developed at Argonne National Laboratory. It has these distinguishing features: It is a sodium-cooled, pool-type reactor; that is, all the major components, reactor core, pumps, and heat exchanges are in a large sodium-filled pot) [3]. It employs a metallic fuel, a U-Pu-Zr alloy clad with a stainless steel alloy. It has an integral fuel cycle, whereby discharged core and blanket materials can be processed and refabricated in an on-site facility.

We previously have reported experiments using an engineering-scale electrorefiner [4]. The electrorefiner consisted of a cadmium anode or anodic dissolution baskets, solid and liquid cathodes, and a molten salt electrolyte (LiCl-KCl) at 500°C. A dual cathode approach was adopted where uranium is recovered on a solid cathode mandrel and uranium-plutonium is recovered in a liquid cadmium cathode. In the engineering-scale electrorefiner, we have demonstrated the following: electrotransport of uranium from the cadmium anode to a solid cathode in 10-kg batches; anodic dissolution of 10-kg batches of chopped fuel (U-10 wt % Zr); and recovery of 4 kg of heavy metal using the liquid cadmium cathode.

The process will be demonstrated with spent metal fuel in the Fuel Cycle Facility (FCF) attached to the EBR-II reactor at the Argonne-Idaho site. This facility was built in the 1960s and used to demonstrate the closed fuel cycle with uranium-alloy metal fuel during the period 1964-1969 [5].

During this electrorefining process, the concentrations of alkali, alkaline earth, and rare earth fission products in the salt in the electrorefiner must be reduced to lower the amount of heat generated therein. A heavy metal drawdown step (an operation to reduce the heavy metal concentration in the salt) is required before removing the fission products from the salt.

EXPERIMENTAL EQUIPMENT

Electrorefiner Assembly

An engineering-scale electrorefining facility that can support 10 kg of uranium on a single solid cathode was constructed to demonstrate the electrolytic transport of uranium at plant-scale levels and to measure the dissolution rate of clad segments of uranium-zirconium alloy. The electrorefiner assembly is enclosed by a 42-cubic-meter, argon-filled glovebox (with ovens, transfer locks, wells, and lifting systems), that is equipped to control gas pressure, temperature, and gas purity.

Schematic of Drawdown Operation

A schematic representation of the drawdown operation is shown in Fig. 1. A lithium-cadmium alloy (5.8 wt % lithium) that is solid at 500°C is loaded into the anodic dissolution baskets and rotated at 75 rpm; current is driven from the anodic dissolution baskets to a solid mandrel cathode that has a ceramic catch crucible below to collect product that falls off of the solid cathode. Salt and cadmium mixers are operated at 150 and 50 rpm, respectively. The possible drawdown reactions include (1) electrotransport of lithium to the solid cathode and lithium reduction of the uranium and rare earth chlorides at the solid cathode and (2) lithium reduction of the uranium and rare earth chlorides at the anode and electrotransport of the uranium and rare earths to the solid cathode. The design criteria that had to be met for the drawdown equipment include the following: (1) control of the reduction rate by lithium, (2) good separation between uranium and rare earths, and (3) the capability to collect uranium and rare earths over a wide range of salt concentrations.

EXPERIMENTAL RESULTS

The concentrations of uranium in the cathode deposits from the drawdown runs were found to fall into three ranges: low (<0.1 wt %), medium (31.8-39.2 wt %) and high (70-89.3 wt %). The results are summarized in Table I.

Table I. Summary of Data from Drawdown Operations in the Engineering-Scale Electrorefiner

U in Cathode Deposit, wt %	U in Salt, wt %	Run	Rare Earths, wt %
High			
89.3	4.33	65	<0.01
79.5	1.75	71	1.2
73.2	6.68	58	<0.01
70.0	2.98	70	1.1
Medium			
39.2	0.72	75	1.8
32.4	0.14	76	2.7
31.8	1.3	72	2.8
Low			
<0.1	0.015	77	31.8

1. High Uranium Concentration

The average uranium concentrations in the salt during drawdown Runs 58, 65, 70, and 71 ranged from 6.68 to 1.75 wt %, while the concentrations of uranium in the cathode deposits from these runs ranged from 70.0 to 89.3 wt %. These data are plotted in Fig. 2. The concentrations of rare earths (cerium, neodymium, and yttrium) in the cathode deposits were low (1.2 wt % or less). These results are shown in Fig. 3. A description of Run 65 is given below and is typical of the results for the other tests over this range of uranium concentration in the salt and in the cathode deposit.

Run 65. In this test, 4.587 kg lithium-cadmium alloy was loaded into the anodic dissolution baskets. Uranium was removed from the salt and collected on a solid mandrel cathode. During the run, the anodic dissolution baskets and the solid mandrel cathode were rotated at 75 rpm and 20 rpm, respectively. The salt and cadmium mixers were not operated during this run. The dissolution-electrodeposition time was 9.9 h and the average current was 97.8 A. The range of current throughout the run was 90-100 A. The resistance increased from about 12 mΩ to 14 mΩ as the lithium-cadmium alloy was dissolved; the 1.3 V cutoff was reached at the end of the run.

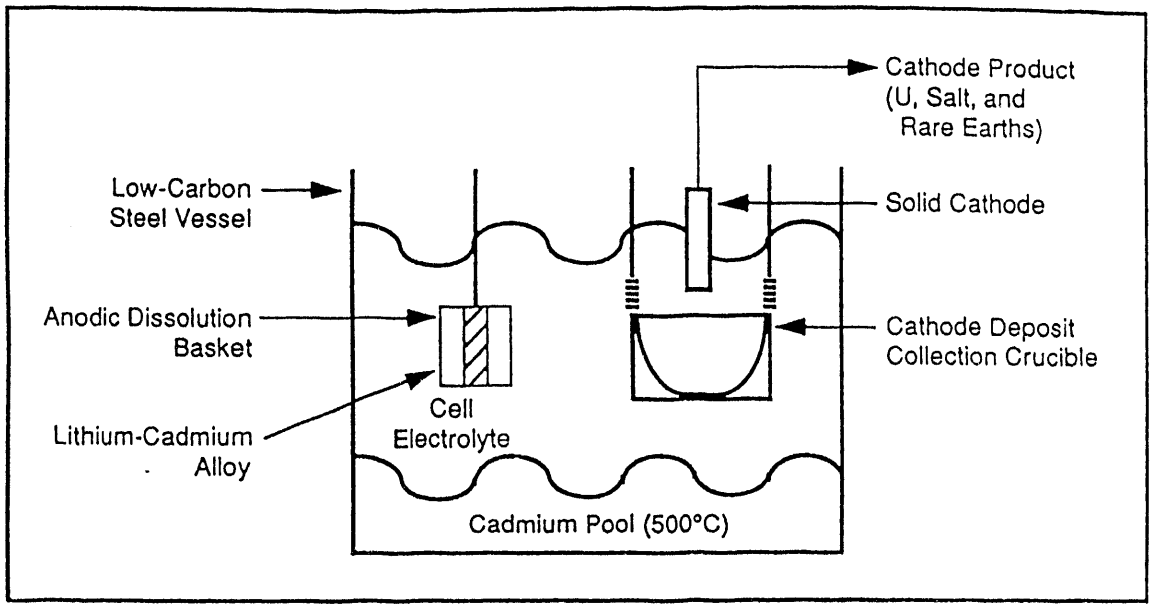

Fig. 1. Schematic of Electrorefiner Drawdown

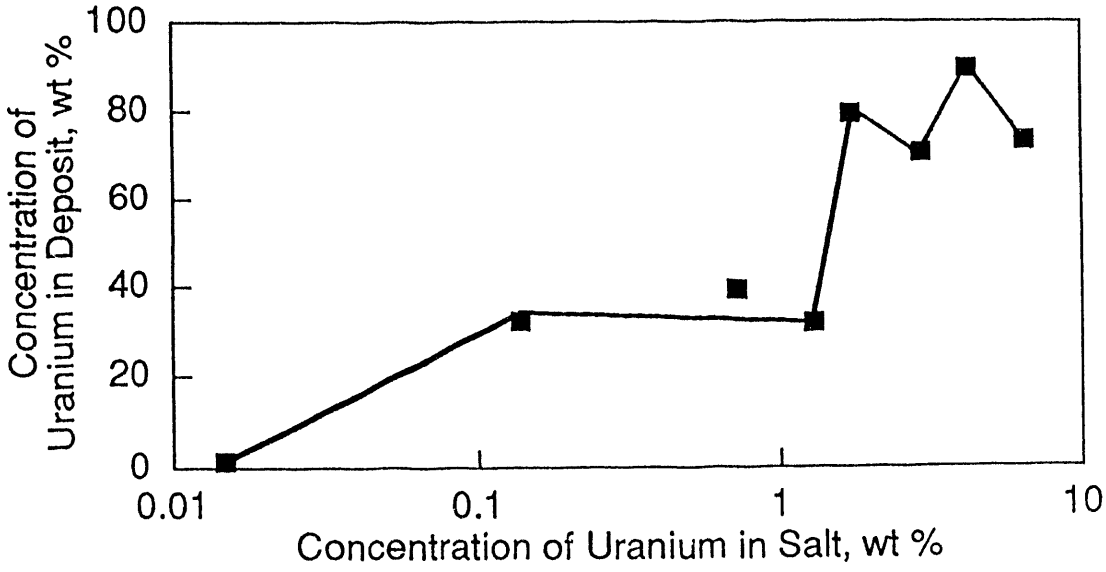

Fig. 2. Uranium Concentration in the Salt vs.
Uranium Concentration in the Cathode Product

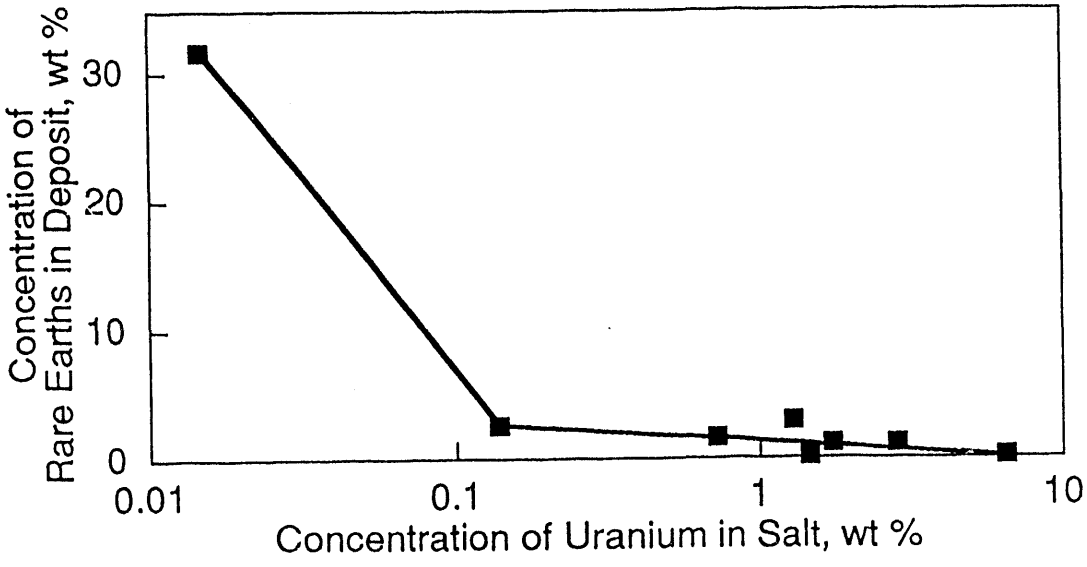

Fig. 3. Concentration of Uranium in the Salt vs.
Concentration of Rare Earths in the Product

A typical dendritic uranium deposit, shown in Fig. 4, was produced. The product weighed 2.0 kg, of which 1.8 kg was uranium. The product composition was 89.3 wt % uranium, 16.5 wt % salt, and 0.14 wt % zirconium. The collection efficiency (59%) on the solid mandrel cathode was slightly higher than normal (typically 40-50%) for electrodeposition on a solid mandrel cathode. The collection efficiency is the ratio of the weight of uranium collected on the solid cathode to the theoretical weight of uranium that would have been collected based on the electrodeposition current (ampere-hours).

The following characteristics of Run 65 were favorable:

1. The uranium drawdown collection rate was 0.2 kg of uranium per hour.

2. The uranium concentration in the cathode product was high and the zirconium concentration was low.

3. The uranium collection efficiency was slightly higher than normal.

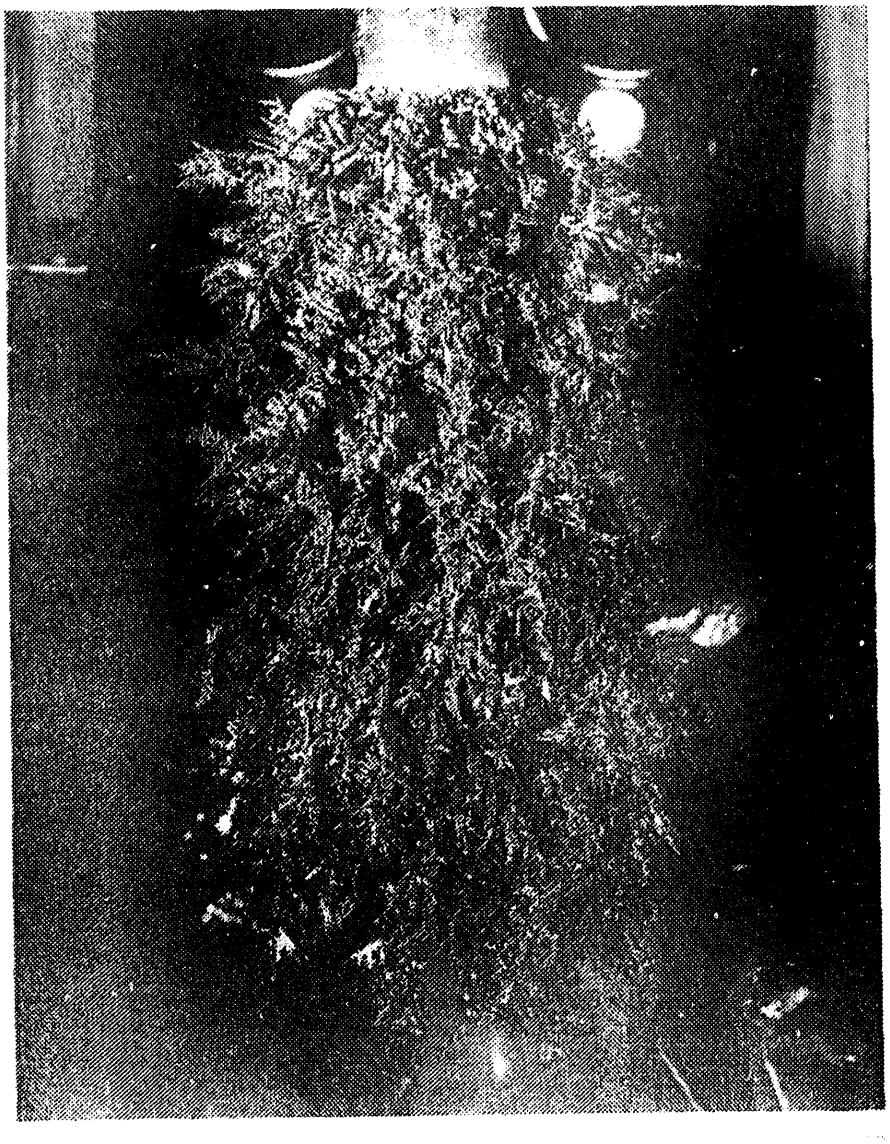

Fig. 4. Cathode Deposit from Drawdown Run 65
(ANL Neg. No. 11790K)

2. Medium Uranium Concentration

The range of average uranium concentrations in the salt during drawdown Runs 72, 75, and 76 was 0.14 to 1.30 wt %. The range of uranium concentrations in the cathode deposits from these runs was 31.8 to 39.2 wt %. These results are plotted in Fig. 2. Run 75 is described below and is typical of the results for the other tests over this range of uranium concentration in the salt and in the cathode deposit. The concentrations of rare earths in the cathode deposits from Runs 72, 75, and 76 were 2.8, 1.8, and 2.7 wt %, respectively. These results are shown in Fig. 3. Over this range of uranium concentration in the salt, the concentrations of rare earths in the cathode deposits were still low (1.8 to 2.8 wt %, as shown in Fig. 3).

Run 75. In this test, 3.050 kg lithium-cadmium alloy was loaded into the anodic dissolution baskets and used to electrotransport uranium from the salt to the tip (steel probe) of the liquid cadmium cathode (LCC) dendrite breaker, which was positioned above an alumina crucible. No cadmium was loaded into this crucible. The mixing conditions for this run were as follows: (1) the cadmium pool and salt mixers were operated at 50 and 75 rpm, respectively; (2) the rotation speed of the anodic dissolution baskets was 75 rpm; and (3) the rotation speed of the LCC dendrite breaker was 15 rpm.

The drawdown operating time was 69 h. The operating voltage was typically 1.2 V, and the resistance was between 100 and 200 mΩ. The average current for Run 75 was 10.3 A, about 25% of that used in the previous drawdown test (Run 72, 39.1 A average current), in which product was collected on the solid mandrel cathode. This lower current resulted from the lower initial cathode area (15.5 cm^2) used in Run 75 compared with Run 72 (476.6 cm^2).

The cathode product collected in Run 75 is shown in Figs. 5 and 6. Figure 5 shows the assembled cathode crucible, the product, and the dendrite breaker, to the tip of which a small amount of product is still attached. Most of the product fell off the breaker and into the alumina crucible. The paste-like characteristic of the product is evidenced by the impression of the tip of the dendrite breaker on the surface of the deposit. The alumina collection-crucible had broken away from the product, and the sectioned product is shown on Fig. 6. A slit in the alumina crucible allowed the salt in the upper half of the deposit to drain off. The product did not slump.

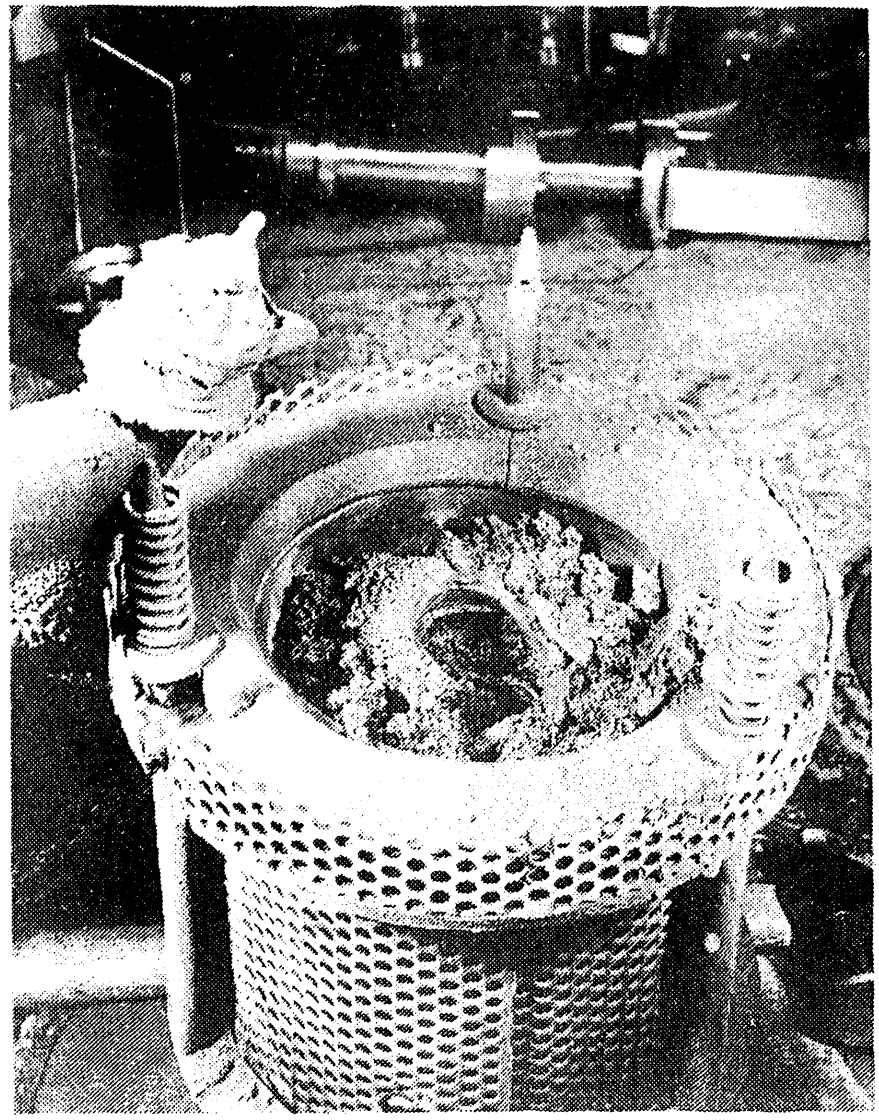

Fig. 5. Crucible Cathode Product and Dendrite Breaker from Run 75
(ANL Neg. No. 12206K)

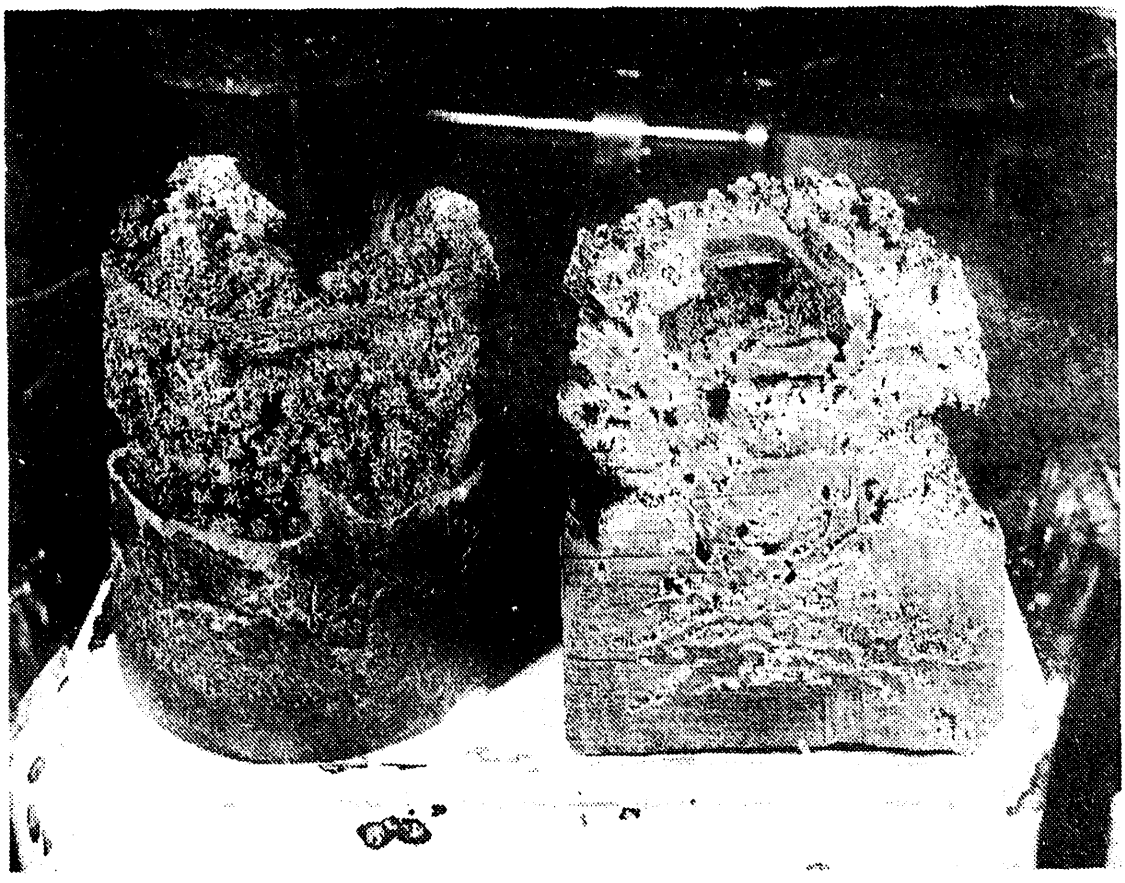

Fig. 6. Sectioned Cathode Product from Run 75
(ANL Neg. No. 1250K)

The cathode deposit weighted 4.90 kg. It was 5.50 in (13.97 cm) in diameter and 6.75 in. (17.15 cm) high. Top, middle, and bottom samples were taken from the product and submitted for chemical analysis, which showed that it contained 39.2 wt % uranium, 63.6 wt % salt, 0.9 wt % cerium, 0.8 wt % neodymium, 0.1 wt % yttrium, and 0.05 wt % zirconium. This deposit contained a higher concentration of salt than drawdown runs made with the upper range of uranium concentration in the salt.

3. Low Uranium Concentration

The average concentration of uranium in the salt during drawdown Run 77 was 0.015 wt %, and the concentration of uranium in the cathode deposit from this run was <0.1 wt %. This result is also plotted in Fig. 2. The concentration of rare earths in the deposit was 31.8 wt %, which is shown in Fig. 3.

In Run 77, uranium and rare earths were electrotransported from the salt to a solid mandrel cathode using 3.539 kg lithium-cadmium alloy that was loaded into the anodic dissolution baskets. The operating time of the run was 21.8 h and the average current was 32.8 A. The operating voltage was typically 1.1 V and the resistance was 30 to 40 mΩ.

The cathode product collected in Run 77 is shown in Figs. 7 and 8. About 40% of the product adhered to the solid mandrel cathode. The smooth product at the tip of the mandrel shows the paste-like characteristics of the deposit. The material did not slump when the salt drained away.

The catch crucible collected about 60% of the product in Run 77 and is shown in Fig. 8. A slit in the side of the alumina crucible allowed the salt to run off. The impression of the rotating mandrel is clearly visible at the surface of the deposit, additional evidence of the paste-like characteristics.

The deposit collected in Run 77 weighed 3.0 kg and was 31.8 wt % rare earths (17.7 wt % cerium, 9.8 wt % neodymium, and 4.3 wt % yttrium), 79.6 wt % salt, 0.6 wt % uranium, and <0.01 wt % zirconium. The rare earth concentration in this deposit is higher than that in any of the deposits collected in previous drawdown runs, but the uranium concentration in this deposit was lower than that measured in any of the previous drawdown runs. After drawdown Run 77, cadmium chloride was added to the electrorefiner to oxidize uranium and rare earths that were transported from the salt to the cadmium pool or to the vessel wall in the drawdown operations. Following each of two oxidation steps, lithium-cadmium alloy was added to the electrorefiner in the anodic dissolution baskets to complete the electrotransport of uranium and rare earths in the salt to a solid mandrel cathode. After these operations, the uranium concentration in the salt was reduced to 0.05 ppm and the rare earth concentration was reduced to less than 0.01 wt %. The zirconium concentration in the deposit is very low (<0.01 wt %).

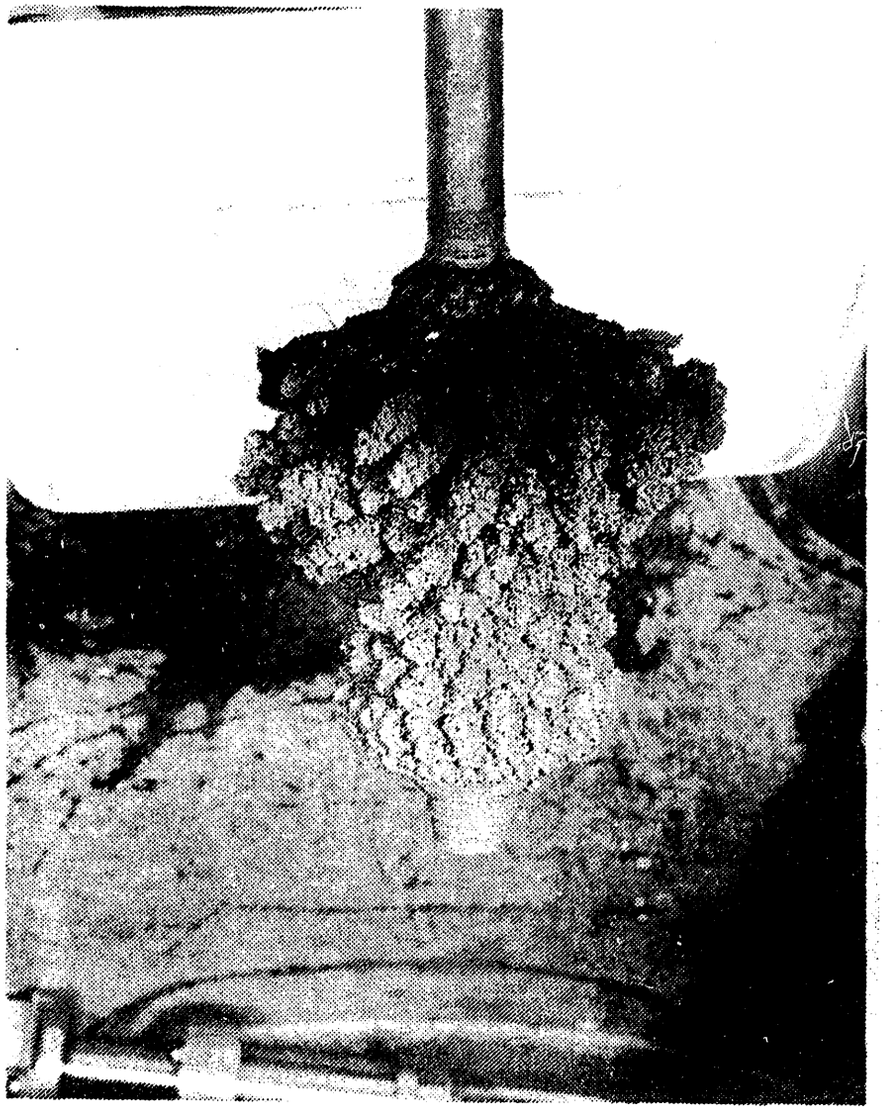

Fig. 7. Solid Mandrel Cathode and Deposit from Drawdown Run 77
(ANL Neg. No. 12352K)

Fig. 8. Catch Crucible and Product from Drawdown Run 77
(ANL Neg. No. 12351K)

CONCLUSIONS

Good separation can be achieved while removing uranium and rare earths in the salt from the engineering-scale electrorefiner. Only 13% of the rare earths were removed, while 99.9% of the uranium in the salt was removed. The uranium and rare earth concentrations in the salt were reduced to 0.05 ppm and <0.01 wt %, respectively, using the in-situ drawdown techniques described in this paper. Drawdown tests will be performed in a laboratory-scale electrorefiner (100-300 g batch heavy metal) to determine the separation between plutonium and rare earths in the salt while removing the heavy metal from the salt.

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